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ART 34 AMDT

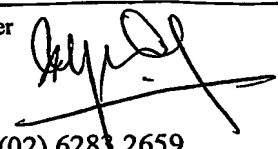
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PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PS220769-142	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/AU2004/000111	International filing date (day/month/year) 30 January 2004	Priority date (day/month/year) 31 January 2003
International Patent Classification (IPC) or national classification and IPC Int. Cl. ⁷ C07D 487/22, C08G 61/12, H01L 31/18		
Applicant UNIVERSITY OF WOLLONGONG OFFICE OF RESEARCH et al		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
 - a. ☒ (sent to the applicant and to the International Bureau) a total of 9 sheets, as follows:
 - ☒ sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
 - ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
 - b. ☐ (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or table related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).
4. This report contains indications relating to the following items:

<input checked="" type="checkbox"/> Box No. I	Basis of the report
<input type="checkbox"/> Box No. II	Priority
<input type="checkbox"/> Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
<input type="checkbox"/> Box No. IV	Lack of unity of invention
<input checked="" type="checkbox"/> Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
<input type="checkbox"/> Box No. VI	Certain documents cited
<input type="checkbox"/> Box No. VII	Certain defects in the international application
<input type="checkbox"/> Box No. VIII	Certain observations on the international application

Date of submission of the demand 24 August 2004	Date of completion of the report 24 March 2005
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer  S.R. IDRUS Telephone No. (02) 6283 2659

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.

PCT/AU2004/000111

Box No. I Basis of the report

1. With regard to the language, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This report is based on translations from the original language into the following language which is the language of a translation furnished for the purposes of:

☐ international search (under Rules 12.3 and 23.1 (b))

☐ publication of the international application (under Rule 12.4)

☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the elements of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

☐ the international application as originally filed/furnished

☒ the description:

pages 2, 6-31 as originally filed/furnished

pages* 1 received by this Authority on 30 November 2004 with the letter of 30 November 2004

pages* 3-5 received by this Authority on 15 March 2005 with the letter of 15 March 2005

☒ the claims:

pages 37-39 as originally filed/furnished

pages* as amended (together with any statement) under Article 19

pages* 32-36 received by this Authority on 15 March 2005 with the letter of 15 March 2005

pages* received by this Authority on with the letter of

☒ the drawings:

pages 1/8 to 8/8 as originally filed/furnished

pages* received by this Authority on with the letter of

pages* received by this Authority on with the letter of

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages

☐ the claims, Nos.

☐ the drawings, sheets/figs

☐ the sequence listing (*specify*):

☐ any table(s) related to the sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

☐ the description, pages

☐ the claims, Nos.

☐ the drawings, sheets/figs

☐ the sequence listing (*specify*):

☐ any table(s) related to the sequence listing (*specify*):

* If item 4 applies, some or all of those sheets may be marked "superseded."

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/AU2004/000111

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1-54	YES
	Claims	NO
Inventive step (IS)	Claims 1-54	YES
	Claims	NO
Industrial applicability (IA)	Claims 1-54	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)

The International Search Report identified the following citations:

- D1 Derwent Abstract Accession No. 2001-234912/24
- D2 Derwent Abstract Accession No. 93-137471/17
- D3 Derwent Abstract Accession No. 93-137483/17
- D4 Derwent Abstract Accession No. 93-169909/21
- D5 STN File CA, Abstract 138:169991
- D6 STN File CA, Abstract 138:79883
- D7 STN File CA, Abstract 136:355747
- D8 STN File CA, Abstract 136:223185
- D9 STN File CA, Abstract 136:53617
- D10 STN File CA, Abstract 136:19977
- D11 STN File CA, Abstract 133:276369
- D12 STN File CA, Abstract 132:101945
- D13 STN File CA, Abstract 130:245642

D1 disclosed polymers obtained by electropolymerization which contain light-activatable units but does not describe a cross-linked pair of polymerizable monomer units, so that the polymers obtained are not electrofunctional unit cross-linked polymers where separate spaced apart strands of the polymer are linked via an electrofunctional unit.

The porphyrin monomers or polymers disclosed in D5, D6, D7 and D8 - D11 do not include cross-linked pair of polymerizable monomer units connected to an electrofunctional unit via linkers providing direct or indirect electronic communication between the polymerizable monomer units and the electrofunctional units.

D12 and D13 disclosed polymerizable monomer units which are nickel metallated meso substituted. Such structures are not within the cope of the polymerizable units of the present invention.

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Supplemental Box

In case the space in any of the preceding boxes is not sufficient.

Continuation of: **Box V**

D2 - D4 disclosed photoreceptor devices which include a layer containing a kind of charge generating or transporting material and electrolytic polymer. The electrolytic polymer is shown to be preferably a five membered heterocyclic compound selected from pyrrole, furan or thiophene. However, these citations do not explicitly disclose the electrolytic polymer being attached to the charge generating or transporting material,

Accordingly, Claims 1-54 are novel in the light of citations **D1 - D13**.

The problem faced by the inventors of the present application is to provide improved conductive electrofunctional polymers, wherein the improvements overcame limitations possessed by previous porphyrin-containing polymers and polymerizable monomers, namely, that immobilisation or integration of the large porphyrin moiety in the polymer has significantly disrupted electronic communication within the polymer. The solution proffered involves polymerisation of selected cross-linked polymerizable monomer units in which there is spacing of the porphyrin moiety provided by linkers. None of the citations **D1 - D13** teaches or fairly suggests this solution.

Accordingly, the claimed subject matter involves inventive step in the light of citations **D1 - D13**.

Polymers of the invention have wide ranging applications including chemical and bio-sensing, solar energy and the like. Accordingly, the invention as defined in Claims 1-54 is industrially applicable.

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JC20 Rec'd PCT/PTO 29 JUL 2005

- 1 -

CONDUCTING POLYMERS WITH PORPHYRIN CROSS-LINKERS

TECHNICAL FIELD

The present invention relates to improvements in conductive electrofunctional polymers, improvements in methods of synthesising such electrofunctional polymers, and
5 the use of such polymers.

BACKGROUND ART

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

10 Porphyrins are interesting molecular structures which provide the basis of the light harvesting capabilities of chlorophyll and the oxygen binding capabilities of heme in addition to possessing electron transfer mediation capabilities.

Porphyrins are one of a number of electrofunctional groups or units capable of participating in electron transfer.

15 The introduction of porphyrin groups into the structure of a polymer is intended to introduce the properties of the porphyrin into the polymer. These properties include metal binding, redox activity, photoactivity and light harvesting. Polymers exhibiting these properties can then be incorporated into or applied to the surfaces of devices. The devices can be used for a range of applications.

20 Procedures that enable porphyrin groups to be immobilised on or integrated in polymer chains are known. This may be achieved by:

- (i) forming copolymers with vinyl monomers,
- (ii) covalently binding porphyrins to preformed polymers, or
- (iii) by polymerising groups (vinyl) attached to a natural or synthetic porphyrin.

25 Porphyrins have also simply been added to conducting polymer mixtures.

The synthesis and application of porphyrin containing polymers has been reviewed (Bao, Z.; Yu, L. Trends in Polymer Science, 1995, 3, 159 and references cited therein).

A particularly interesting process involves attachment of electropolymerisable groups to porphyrins. The products of this process can then be used to form a thin coating
30 of the polymeric material on electrodes such as platinum or ITO glass.

Using porphyrin-containing monomers, insoluble films can be electrodeposited and the devices produced used for a range of applications, including electrocatalysis, chemical and biosensing, or solar energy conversion.

Other electrofunctional units include tetranitrogen-containing macrocycles derived from the tetrapyrroles porphin, chlorins and corrins as referred to in DE 42 42 676 A1.

According to a first aspect, the invention consists in a cross-linked pair of polymerisable monomer units having the structure:



where Q and Q' are the polymerisable monomer units, P is an electrofunctional unit and L and L' are linkers providing providing direct or indirect electronic communication between Q and P and between P and Q', and wherein n = 1, 2 or 3 and m = 1, 2 or 3.

Preferably Q and Q' are heteroaromatic rings of the general formula

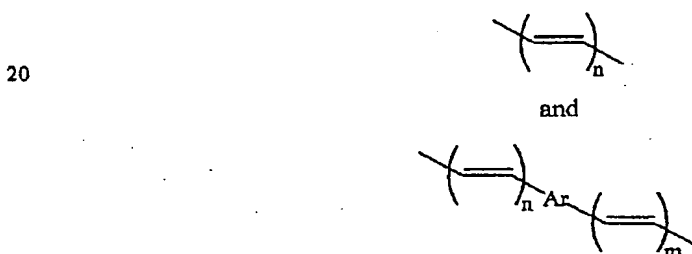


where R can be any suitable polymerisable or non-polymerisable functional group and X can be selected from S, NH or O. Suitable heteroaromatics include: thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

More preferably Q and Q' are of molecular dimensions that permit polymerisation of the monomer units of the cross-linked polymerisable monomer units as a homopolymer.

Q and Q' may be the same or different, preferably Q and Q' are the same.

Preferably the linkers L and L' are selected from the group comprising:



wherein n = 0, 1, 2 or 3, m = 0, 1, 2 or 3, and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich
25 complex.

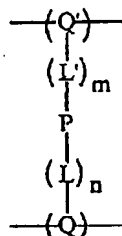
- 4 -

L and L' may be the same or different, preferably L and L' are the same.

Preferably the electrofunctional unit P is selected from the group comprising: porphyrin, substituted porphyrin, phthalocyanine, substituted phthalocyanine or other tetranitrogen-containing macrocycle.

- 5 The electrofunctional unit P may or may not be coordinated to metals. Preferably the electrofunctional unit is coordinated to metal. Preferably the metal is zinc.

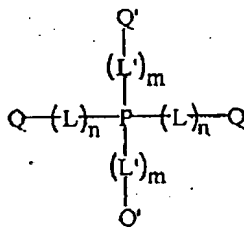
According to a second aspect, the invention consists in an electrofunctional unit cross-linked polymer comprising the structure:



- 10 where P is the electrofunctional unit, Q and Q' are monomer units of the polymer L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q', and wherein n = 0, 1, 2 or 3, m = 0, 1, 2 or 3, and the polymer is a copolymer when m and n = 0.

- 15 The preferments of Q and Q', L and L', and P are the same as the preferments for the first aspect, excluding the preferment that Q and Q' are of molecular dimensions that permit polymerisation of the monomer units of the cross-linked polymerisable monomer units as a homopolymer.

According to a third aspect, the invention consists in a cross-linked quartet of polymerisable monomer units having the structure:

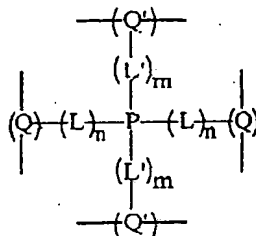


20

where P is an electrofunctional unit, Q and Q' are the polymerisable monomer units, and L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q', and wherein n = 1, 2 or 3 and m = 1, 2 or 3.

The preferments of Q and Q', L and L', and P are the same as the preferments for the first aspect.

According to a fourth aspect, the invention consists in an electrofunctional unit cross-linked polymer comprising the structure:



5

where P is the electrofunctional unit, Q and Q' are monomer units of the polymer, L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q', and wherein n = 0, 1, 2 or 3, m = 0, 1, 2 or 3, and the polymer is a copolymer when m and n = 0.

10 The preferments of Q and Q', L and L', and P are the same as the preferments for the first aspect, excluding the preferment that Q and Q' are of molecular dimensions that permit polymerisation of the monomer units of the cross-linked polymerisable monomer units as a homopolymer.

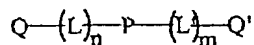
According to a fifth aspect, the invention consists in an electrofunctional unit cross-linked polymer according to the second aspect of the invention wherein the polymer is a copolymer of the monomer units Q and Q' and at least one other monomer unit. Preferably the other monomer unit is a substituted aromatic or heteroaromatic ring. More preferably the other monomer unit is selected from the group comprised of: benzene, substituted benzene, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

25 According to a sixth aspect, the invention consists in an electrofunctional unit cross-linked polymer according to the fourth aspect of the invention wherein the polymer is a copolymer of the monomer units Q and Q' and at least one other monomer unit. Preferably the other monomer unit is a substituted aromatic or heteroaromatic ring. More preferably the other monomer unit is selected from the group comprised of: benzene, substituted benzene, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

According to a seventh aspect, the invention consists in a cross-linked pair of monomer units, cross-linked quartet of monomer units, polymer, or copolymer according to

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A cross-linked pair of polymerisable monomer units having the structure:



where Q and Q' are polymerisable units

- 5 L and L' are linkers providing direct or indirect electronic communication between P and Q and Q'

P is an electrofunctional unit

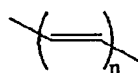
wherein n = 1, 2 or 3

wherein m = 1, 2 or 3

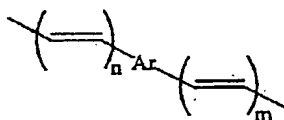
- 10 2. A cross-linked pair of polymerisable monomer units according to claim 1 wherein Q and Q' are substituted aromatic rings or heteroaromatic rings selected from the group comprising:

substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

- 15 3. A cross-linked pair of polymerisable monomer units according to claim 1 or claim 2 wherein L and L' are selected from the group comprising:



and



- 20 wherein n = 1, 2 or 3

wherein m = 1, 2 or 3

and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.

- 25 4. A cross-linked pair of polymerisable monomer units according to any one of the preceding claims where P is selected from the group comprising:

porphyrin

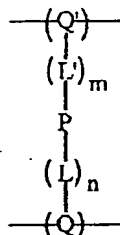
substituted porphyrin

phthalocyanine

substituted phthalocyanine

tetranitrogen-containing macrocycle

5. A cross-linked pair of polymerisable monomer units according to any one of claims 1 to 4 wherein Q and Q' are of molecular dimensions sufficient to permit polymerisation of the monomer units of the cross-linked pair of polymerisable monomer units as a homopolymer.
6. An electrofunctional unit cross-linked polymer comprising the structure:



where Q and Q' are monomer units of the polymer

L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q'

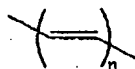
P is an electrofunctional unit

wherein $n = 0, 1, 2$ or 3 , $m = 0, 1, 2$ or 3 , and the polymer is a copolymer when m and $n = 0$.

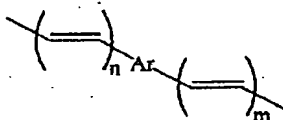
7. An electrofunctional unit cross-linked polymer according to claim 6 wherein Q and Q' are substituted aromatic rings or heteroaromatic rings selected from the group comprising:

substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

8. An electrofunctional unit cross-linked polymer according to claims 6 or claim 7 wherein L is selected from the group comprising:



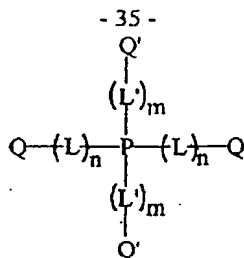
and



wherein $n = 0, 1, 2$ or 3 , $m = 0, 1, 2$ or 3 , and the polymer is a copolymer when m and $n = 0$.

and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.

9. An electrofunctional unit cross-linked polymer according to any one of claims 6 to 8 wherein P is selected from the group comprising:
5 porphyrin
substituted porphyrin
phthalocyanine
substituted phthalocyanine
10 tetranitrogen-containing macrocycle
10. An electrofunctional unit cross-linked polymer according to any one of claims 6 to 9 wherein the polymer is a copolymer of the monomer units Q and Q' and at least one other monomer unit.
11. An electrofunctional unit cross-linked polymer according to claim 10 wherein the
15 other monomer unit is a substituted aromatic or heteroaromatic ring.
12. An electrofunctional unit cross-linked polymer according to claim 11 wherein the other monomer unit is selected from the group comprising:
substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.
- 20 13. An electrofunctional unit cross-linked polymer according to claim 12 wherein the other monomer unit is terphenyl.
14. An electrofunctional unit cross-linked polymer according to any one of claims 6 to 13 wherein the electrofunctional unit is coordinated with metal.
15. An electrofunctional unit cross-linked polymer according to claim 14 wherein the
25 metal is zinc.
16. An electrofunctional unit cross-linked polymer according to any one of claims 6 to 15 wherein the polymer has been prepared by electropolymerisation.
17. A cross-linked quartet of polymerisable monomer units having the structure:



wherein:

Q and Q' are the polymerisable monomer units

L and L' are linkers providing direct or indirect electronic communication between

5 P and Q and Q'

P is an electrofunctional unit

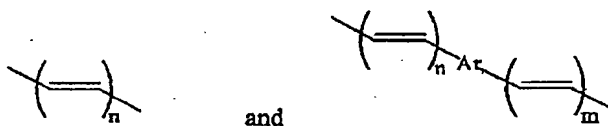
n = 1, 2 or 3

m = 1, 2 or 3

18. A cross-linked quartet of polymerisable monomer units according to claim 17
10 wherein Q and Q' are substituted aromatic rings or heteroaromatic rings selected from the group comprising:

substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

19. A cross-linked quartet of polymerisable monomer units according to claim 17 or
15 claim 18 wherein L is selected from the group comprising:



wherein n = 1, 2 or 3, m = 1, 2 or 3, and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.

20 20. A cross-linked quartet of polymerisable monomer units according to claim 17 or claim 18 where P is selected from the group comprising:

porphyrin

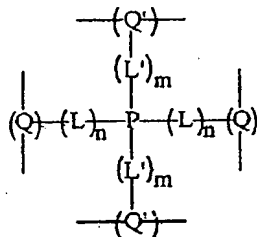
substituted porphyrin

phthalocyanine

25 substituted phthalocyanine

tetranitrogen-containing macrocycle

21. A cross-linked quartet of polymerisable monomer units according to any one of claims 17 to 20 wherein Q and Q' are of molecular dimensions sufficient to permit polymerisation of the monomer units of the cross-linked quartet of polymerisable monomer units as a homopolymer.
- 5 22. An electrofunctional unit cross-linked polymer comprising the structure:



where Q and Q' are monomer units of the polymer

L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q'

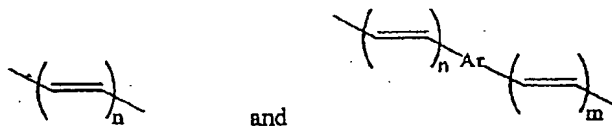
10 P is the electrofunctional unit

wherein $n = 0, 1, 2$ or 3 , $m = 0, 1, 2$ or 3 , and the polymer is a copolymer when m and $n = 0$.

23. An electrofunctional unit cross-linked polymer according to claim 22 wherein Q and Q' are substituted aromatic rings or heteroaromatic rings selected from the group comprising:
- 15

substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

24. An electrofunctional unit cross-linked polymer according to claims 22 or claim 23 wherein L is selected from the group comprising:



20

wherein $n = 0, 1, 2$ or 3 , $m = 0, 1, 2$ or 3 , the polymer is a copolymer when m and/or $n = 0$, and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.